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PROPERTIES OF ION-CONDUCTING LANTHANUM LITHIUM TITANATE BASED CERAMICS

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Samples of lanthanum lithium titanate with the general formula $La_{2/3-x}Li_{3x}TiO_3$ with a different vacancy content, which is varied by varying the ratio of lanthanum to lithium, are investigated. Methods of synthesis, neutron diffraction data for the samples obtained, measurements of the lithium-ion conductivity of equilibrium and quenched samples, the results of nuclear magnetic resonance on ^7Li nuclei, the dynamic characteristics of heat release (heat absorption), and the magnetic susceptibility of some samples are presented.

Materials based on lanthanum lithium titanate with perovskite structure have been studied intensively for the last 10 years in virtually all industrially developed countries. Being purely ionic conductors with respect to lithium they are drawing the attention of researchers primarily because these conductors have unique electric properties, making them promising as separators of low- and medium-temperature lithium sources of electric current. The conductivity of samples of materials with the general formula $La_{2/3-x}Li_{3x}TiO_3$ (LLTO) depends strongly on the ration of lanthanum and lithium, since this ratio determines the concentration of cationic vacancies. In a series of works [1 – 3] the formula for the compound is written in the form $La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$, where the symbol $\square$ denotes a cationic vacancy, showing this dependence directly. For $x \sim 0.1$ the compound at room temperature has a lithium-cationic conductivity of approximately 10^{-3} S/cm [1, 2]. In practice, this is the highest ionic conductivity known today at these temperatures in crystalline bodies. The electronic conductivity of materials in air is so low that it cannot measured within the limits of sensitivity of modern instruments.

Materials based on LLTO possess high ceramic characteristics: they press well and sinter at 1200 – 1300°C. This makes it possible to miniaturize devices which are manufactured using LLTO materials. Articles made from raw materials with a low content of cationic impurities with variable valence have a dull white color.

The present article presents the results of investigations of the effect of the structural and thermal properties and the cooling regimes of the samples on the ionic conductivity of LLTO. To this end the samples were obtained under equilibrium conditions or quenched in air and liquid nitrogen.

The samples were synthesized using the well-known ceramics technology [1, 2]. Calcined powders served as the initial materials: chemically pure La_2O_3, pure TiO_2, and chemically pure Li_2CO_3. Weighed batches were mixed in an agate mortar, pressed at pressure 200 – 220 MPa into 13 mm in diameter and 3 – 5 mm thick pellets. The pellets were placed into a corundum crucible and a Silit furnace. Synthesize was conducted in air in four stages. At the first stage the samples were calcined at 900°C for 9 h. After cooling they were ground and pressed once again under the same pressures. Subsequent calcinations were performed at 1200°C for 24 h with intermediate millings of the materials. The final cooling of the samples was conducted at a rate of no more than 0.4 K/min to avoid quenching the structure.

The porosity of the samples was calculated by comparing the apparent and x-ray densities of the materials. The porosity of the $La_{2/3-x}Li_{3x}TiO_3$ samples obtained with different cooling conditions is presented in Table 1. It is evident that the samples prepared using this technology had an average porosity of 10 – 15 vol.%.

The vacancy concentration in the cationic sublattice of the compound was set by adhering to the exact ratio of the La and Li concentrations. The lanthanum and lithium content in the samples was monitored by chemical analysis.

The samples were quenched as follows. They were held for 5 h at 1200°C and then dropped into liquid nitrogen or placed onto a massive metal plate. After the samples cooled

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TABLE 1.

Sample	Vacancy content, at. %	Cooling regime, K/min	Porosity, vol.%
1	3	0.4	19.7
2	5	0.4	10.8
3	8	0.4	10.8
4	10	0.4	9.5
5	12	Cooling in air	14.0
6	15	0.4	11.3
7	18	Quenching in nitrogen	12.9
8	20	0.4	15.5
9	24	0.4	29.5

Fig. 1. Temperature dependence of the lattice parameters of $La_{2/3-x}Li_{3x}TiO_3$ with $x = 0.076(6)$, obtained by neutron diffraction.

down their phase composition was investigated. The phase composition of the samples was monitored by x-ray phase analysis using the DRON-3M diffractometer with CuK_α radiation. The investigations showed that such quenching changes the diffraction pattern substantially. Specifically, the peaks corresponding to the superstructure of the lattice vanish; this is seen especially well at small angles. The more symmetric phase of the compound $La_{2/3-x}Li_{3x}TiO_3$ is quenched but a completely cubic phase cannot be obtained. The lines characterizing the tetragonal distortion of the lattice remain in the x-ray diffraction patterns.

Detailed structural investigations of the unquenched samples were performed by means of neutron diffraction. In particular, the temperature changes of the lattice parameters were studied (Fig. 1). Up to 300°C all parameters vary isotropically. At higher temperatures the parameter c increase more rapidly than the parameters a and b. This indicates substantial restructuring of the lattice of the compound obtained by slow cooling in the direction of tetragonality, especially noticeable at temperatures above 300°C.

Specific heat of the unquenched samples was measured with a NETZSCH STA 449C analyzer in the range from room temperature to 1000°C in purified argon as the purging gas blown through at 10 ml/min. The electrolyte in the form of pressed and calcined $3 \times 3 \times 2$ mm samples was placed in a calibrated corundum crucible. The heat effects and mass losses of the samples were measured simultaneously on the setup, and built-in programs automatically calculated the quantities required.

The errors were 0.2 wt.% in determining the mass and no more than 0.5% for the thermal quantities. The largest mass losses recorded in the experiments on samples with different mass did not exceed 0.8%, so that these losses can be correlated to the removal of surface impurities rather than to the volatilization of the components of the compound.

The temperature dependences of the specific heats were measured with different rates of temperature increase to determine the closeness of the heat effects to equilibrium (Fig. 2). It is evident from the data obtained that the com-
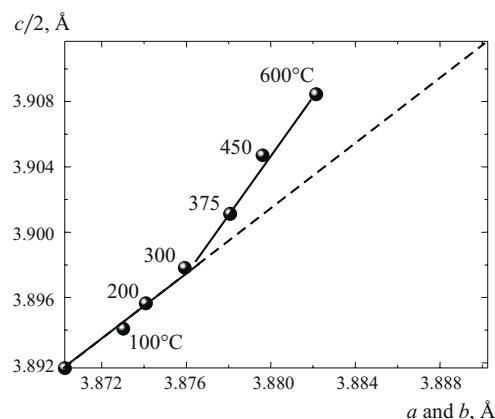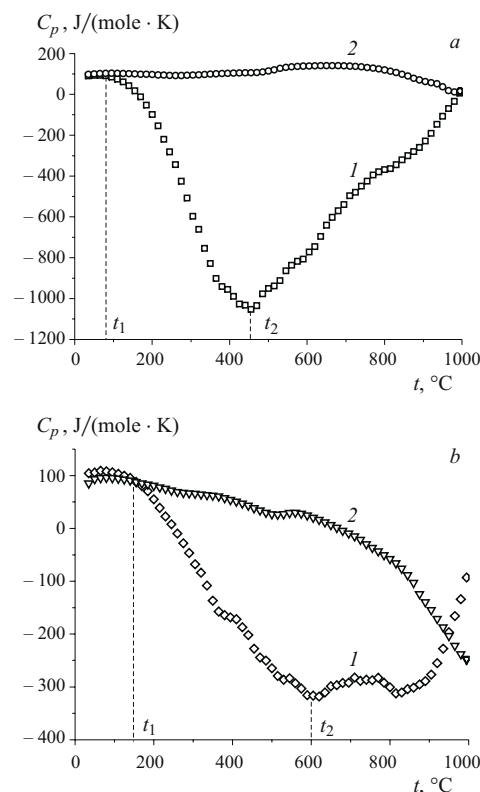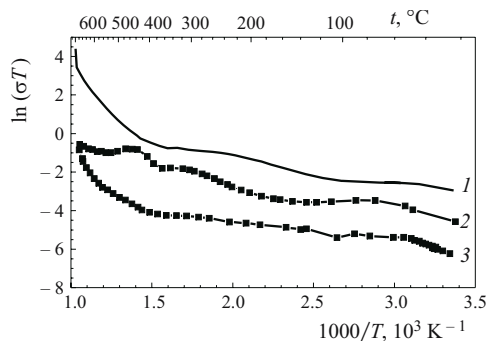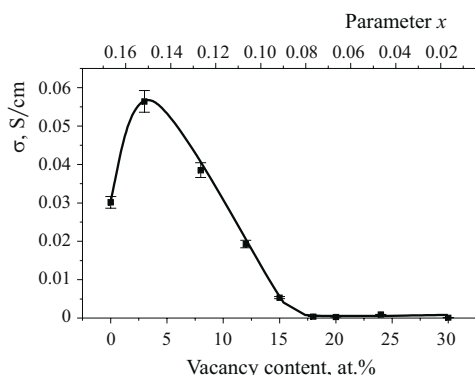

Fig. 2. Temperature dependences of the specific heat C_p of the compound $La_{2/3-x}Li_{3x}TiO_3$: *a*) $x = 0.166(6)$; *b*) $x = 0.126(6)$; *1, 2*) heating rates 1 and 10 K/min, respectively.

pleteness of the heat effects depends on the rate of temperature increase and even at 1 K/min nonequilibrium values of the specific heat are measured in the indicated compound.

A standard DTA curve obtained for the sample $La_{2/3-x}Li_{3x}TiO_3$ with $x = 0.166(6)$, using a Q-1500D derivatograph up to 1000°C also confirms the presence of heat effects in LLTO. The heat effects on the DTA curves are dif-
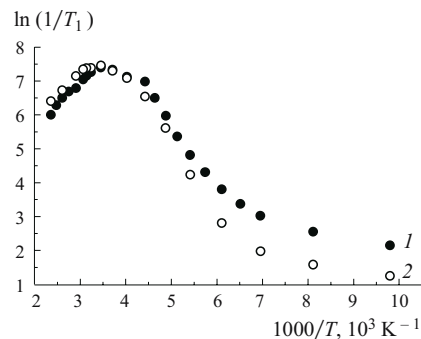
Fig. 3. Temperature dependences of the ionic conductivity (σT, S · cm^{-1} · K) of La$_{2/3-x}$Li$_{3x}$TiO$_3$ samples with $x = 0.076(6)$: *1*) unquenched sample; *2, 3*) quenched sample, heating and cooling, respectively.

Fig. 5. Temperature dependence of the spin-lattice relaxation rates ($1/T_1$, sec^{-1}) of ^{7}Li nuclei in the compound La$_{2/3-x}$Li$_{3x}$TiO$_3$ with $x = 0.1416(6)$: *1, 2*) at the working frequencies of the magnetic oscillations 13 and 35 MHz, respectively.

Fig. 4. Conductivity of equilibrium samples of La$_{2/3-x}$Li$_{3x}$TiO$_3$ versus the vacancy concentration at 300°C.

fuse but they provide qualitative confirmation of the results obtained in previous investigations.

The electric conductivity was measured with an E7-14 ac current bridge at 10 kHz, dividing the impedance of the cells by the volume resistance and capacitive reactance. Silver electrodes were used to perform the measurements on the unquenched samples, and gallium-silver paste electrodes, which were deposited on the end surfaces of the samples, were used when working with quenched samples. The measurements were performed in air with forward and backward variation of the temperature and for rates of heating-cooling of the samples at equilibrium of not more than 0.4 K/min with the samples held at each measurement point for 0.5 h. When measurements were performed on the quenched samples the rate of heating was increased to 1 K/min, and the holding time at the temperature points of the conductivity measurements was decreased substantially. The accuracy of the conductivity measurements under equilibrium conditions was 10% of the measured value. The results obtained are presented in Fig. 3. Quenching the samples reduces the ionic conductivity σ of the compound LLTO substantially in the entire temperature range. The high lithium cationic conductivity of unquenched samples of the compound at room temperature, equal to 1.6×10^{-3} S/cm, is attractive. Today this is the highest conductivity among known solid electrolytes.

Next, the dependence of the conductivity of unquenched samples of the compound on the concentration of cationic vacancies was investigated. Their content in the solid electrolyte, whose formula is usually written in the form La$_{2/3-x}$Li$_{3x}$□$_{1/3-x}$TiO$_3$ [2, 3], was set by varying the lanthanum and lithium fractions in the cationic sublattice (the symbol □ denotes vacancies in the cationic sublattice of the compound). The vacancy concentration range was varied from $\sim 1 \times 10^{-2}$, corresponding to intrinsic defects at a fixed temperature, to 0.30 atomic fractions of the cationic sublattice. The concentration dependences obtained for the electric conductivity of unquenched LLTO samples have the same form up to 700°C (Fig. 4).

NMR on ^{7}Li nuclei was used to investigate for unquenched samples the temperature dependences of the spin-lattice relaxation rates, which were used to calculate the activation energy of short-range motion of lithium carriers. The investigations were performed by the pulse method at 13 and 35 MHz and heating up to the required temperatures stopping as necessary to perform measurements.

The results of the rate measurements are presented in Arrhenius coordinates in Fig. 5. As one can see, the data for different rates coincide at high temperatures.

The activation energy of short-range motion of the lithium carriers was calculated on the linear sections of the low- and high-temperature parts of the curves (Fig. 5). It was determined that for the measurements performed at high frequencies the activation energy is independent of the frequency and equals 15.0 kJ/mole.

The investigations showed that La$_{2/3-x}$Li$_{3x}$TiO$_3$ crystallizes into a perovskite lattice with tetragonal distortion along the c axis. Quenching samples at temperatures below 1200°C in air or liquid nitrogen results in a small increase of the symmetry of the crystal lattice but does not lift the tetragonal distortion at all. Similar results were obtained in [3], where an attempt was made to stabilize the cubic phase of LLTO by varying the composition and quenching.

Analysis of the data in Fig. 1 suggests a possible reason for this. Up to 300°C all lattice parameters increase at the same relative rate determined by the anharmonic displacement of the particles, while in the range 300 – 600°C the parameter c increases much more rapidly. This attests to a redistribution of the lanthanum between the [0 0 1/2] and [0 0 1] layers of the lattice toward the second layers, which is what the authors of [4] also observed.

The migration of the lanthanum ions is accompanied by vacancies and cations of lithium concentrating in the [0 0 1/2] layers, where conditions are created for superionic conduction. We note that our results all confirm this supposition. In the first place, the specific heat of $La_{2/3-x}Li_{3x}TiO_3$ changes in a definite manner (see Fig. 2). Up to 150 – 200°C the specific heat of all experimental samples is independent of temperature and then it drops sharply to negative values. This attests to heat release by the electrolyte lattice with a decrease of the internal energy, which occurs at the same temperature as the onset of cation migration. The migration of the ions in the cationic sublattice is slow, since the values of the specific heat obtained with the samples heated at different rates are appreciably different. This is also confirmed by the presence of a strongly extended exothermal peak in the DTA curve of the sample $La_{2/3-x}Li_{3x}TiO_3$ with $x = 0.166(6)$ at temperatures above 300°C.

The only possible explanation for heat effects of such a magnitude is lattice restructuring. They cannot be due to, for example, magnetic interactions between [7]Li carriers or atoms of magnetic impurities because the concentrations of such atoms in the samples are very low. This is confirmed by the negligible (D. G. Kellerman performed the measurements) magnetic susceptibility of materials with 91.2 or 7.5 at.% [6]Li (Fig. 6).

In the range 200 – 600°C the samples release heat and the structure of the lattice becomes more ordered as a result of the migration of lanthanum. Heat absorption starts above 600°C. The evidence for this is that the specific heat becomes positive at 1000°C. Since the specific heat varies over an extended range, it can be supposed that in the range 600 – 1000°C two opposing processes compete with one another — residual ordering of lanthanum with transitions in the layers and onset of its chaotic disordering of the lanthanum (intermixing of the layers). Thus, the compound $La_{2/3-x}Li_{3x}TiO_3$ does not have a nonvariant temperature point and is highly prone toward quenching of the structure. The reason for this is the formation of layers of cations in the sublattice and the very slow relaxation rate of such a layered structure during annealing as the data in Fig. 3 confirm: the quenching itself and the heating – cooling cycle produce a lower ionic conductivity, resulting from the slow destruction of a large number of superconducting layers in the electrolyte.

The dependence of the lithium-cation conductivity of unquenched samples on the vacancy concentration in the cationic sublattice (see Fig. 4) attests to the fact that the isotherms possess maxima at vacancy content 3 – 5 at.%. Below
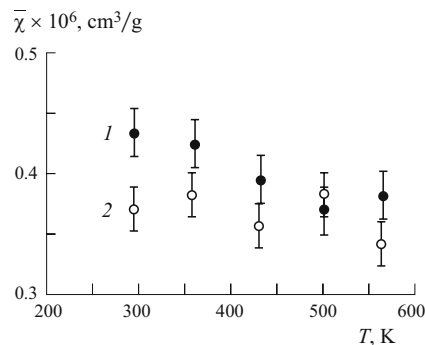
Fig. 6. Temperature dependences of the magnetic susceptibility χ of $La_{2/3-x}Li_{3x}TiO_3$ with $x = 0.166(6)$ and different atomic content of Li isotopes: *1*) 7.5% [6]Li and 92.5% [7]Li; *2*) 91.2% [6]Li and 8.8% [7]Li.

the maximum the conductivity increases because the vacancy concentration increases in the cationic sublattice with a sufficiently large number of lithium carriers. After the maximum the conductivity drops appreciably, probably because the number of lithium ions decreases while the number of vacancies is large. Apparently, this ratio between the vacancies and lithium is optimal at the maximum.

The interaction of carriers with one another as they move in crystals also decreases the ionic conductivity. The characteristics of short- and long-range motion of the lithium carriers can be used to determine the degree of correlation of their motion of these in this electrolyte. In particular, the activation energy for short-range motion, equaling 15.0 kJ/mole, is close to the activation energy (20.0 kJ/mole) of long-range motion, calculated from data on the conductivity at low temperatures (200°C). This means that at low temperatures the lithium ions interact weakly with one another and move predominately as independent current carriers with small energy losses. Since at low temperatures the lithium ions and vacancies are concentrated in the [0 0 1/2] layers, it can be supposed that, apparently, the optimal ratio of the vacancy and carrier concentrations in the layers and no interaction between moving carriers are the physical essence of the superionic state of a solid electrolyte. These favorable conditions occur at low temperatures in a lattice of this compound and give rise to such a high lithium-cationic conductivity.

Sharp growth of the conduction activation energy (up to 60.0 kJ/mole) with increasing temperature is observed in unquenched samples (see Fig. 3). This is probably due to the destruction of the superconducting layers because of intense interlayer transitions [0 0 0] $\rightleftarrows$ [0 0 1/2] of lanthanum cations and, correspondingly, a redistribution of vacancies and lithium. The temperature dependence of the specific heat supports this conjecture (see Fig. 2): at temperatures 500 – 600°C heat absorption by the sample starts to predominate over internal heat release. The lanthanum and lithium layers with vacancies intermix, the superionic state is lifted, and $La_{2/3-x}Li_{3x}TiO_3$ becomes an ordinary crystal.

In summary, the synthesized samples of the solid electrolyte $La_{2/3-x}Li_{3x}TiO_3$ with different ratios of the lanthanum and lithium ions have a perovskite crystal cell with tetragonal distortion along the c axis.

The compound obtained is a superionic conductor whose room-temperature electric conductivity is approximately 10^{-3} S/cm. The superionic state vanishes at elevated temperatures. Quenching the samples at 1200°C in air and liquid nitrogen decreases the conductivity by a factor of $2 - 5$.

It was determined that the $La_{2/3-x}Li_{3x}TiO_3$ lattice is highly prone to securing high-temperature states with intermixed layers of lanthanum and lithium cations and vacancies. These states relax slowly, transitioning into the initial structure with lanthanum-filled layers and layers which are superconducting with respect to lithium cations. This is the reason for the complex temperature dependences of the conductivity and other physicochemical properties of $La_{2/3-x}Li_{3x}TiO_3$ based ceramic materials.

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